(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 510 224 A1**

(12) EUROPEAN PATENT APPLICATION

(21) Application number: 91106546.7

(51) Int. Cl.5: **C25D 5/10**

(22) Date of filing: 23.04.91

(43) Date of publication of application:
28.10.92 Bulletin 92/44

(84) Designated Contracting States:
DE FR GB

(71) Applicant: **NKK CORPORATION**
1-2 Marunouchi 1-chome, Chiyoda-ku
Tokyo(JP)

(72) Inventor: **Sagiyama, Masaru, c/o NKK Corporation**
1-2, 1-chome Marunouchi, Chiyoda-ku
Tokyo(JP)
Inventor: **Yoshida, Masafumi, c/o NKK Corporation**
1-2, 1-chome Marunouchi, Chiyoda-ku
Tokyo(JP)
Inventor: **Kawabe, Masaki, c/o NKK Corporation**
1-2, 1-chome Marunouchi, Chiyoda-ku
Tokyo(JP)
Inventor: **Ando, Satoru, c/o NKK Corporation**
1-2, 1-chome Marunouchi, Chiyoda-ku
Tokyo(JP)
Inventor: **Ono, Tadashi, c/o NKK Corporation**
1-2, 1-chome Marunouchi, Chiyoda-ku
Tokyo(JP)

(74) Representative: **Henkel, Feiler, Hänzel & Partner**
Möhlstrasse 37
W-8000 München 80(DE)

(54) **Plated steel sheet having two plating layers and excellent in antifriction, corrosion resistance and painting adaptability.**

(57) A plated steel sheet having two plating layers and excellent in antifriction, corrosion resistance and painting adaptability, which comprises: a steel sheet; a zinc plating layer formed on at least one surface of the steel sheet; and an electroplating layer formed on the zinc plating layer. The zinc plating layer has a plating weight of from 25 to 150 g/m^2 per surface of the steel sheet. The electroplating layer comprises at least one element selected from the group consisting of chromium, manganese, iron, cobalt and nickel, and the electroplating layer has a plating weight of from 1 to 10 g/m^2 per surface of the steel sheet.

EP 0 510 224 A1

REFERENCE TO PATENTS, APPLICATIONS AND PUBLICATIONS PERTINENT TO THE INVENTION

As far as we know, there is available the following prior art document pertinent to the present invention: "Plating & Surface Finishing", March 1989, pp. 62-69.

The contents of the prior art disclosed in the above-mentioned prior art document will be discussed hereafter under the heading of the "BACKGROUND OF THE INVENTION".

FIELD OF THE INVENTION

The present invention relates to a plated steel sheet having two plating layers and excellent in antifriction upon press-forming, corrosion resistance and painting adaptability.

BACKGROUND OF THE INVENTION

In general, the body of an automobile is exposed to a corrosive environment, and particularly to a severe corrosive environment in a coastal area or a cold area where an automobile tends to come into contact with a substance containing chlorine ions having a violent corrosivity.

A zinc plated steel sheet or a zinc alloy plated steel sheet is conventionally widely used as a steel sheet for an automobile body having an excellent corrosion resistance even in such a severe corrosive environment.

The conventional zinc plated steel sheet has however the following problems:

(1) The zinc plating layer of the zinc plated steel sheet, having a relatively low hardness, is deformed upon the press-forming of the zinc plated steel sheet, thus increasing a contact area between the zinc plating layer and the pressing portion of a press. In other words, the zinc plated steel sheet has a frictional coefficient higher than that of the other steel sheets such as a cold-rolled steel sheet or a zinc alloy plated steel sheet. When press-forming the zinc plated steel sheet, therefore, cracks may be produced in the zinc plating layer thereof. As is clear from the above description, the conventional zinc plated steel sheet is poor in antifriction (hereinafter referred to as the "problem 1"); and

(2) When applying an electropainting to the zinc plated steel sheet to form a painting film on the surface thereof, the high hydrogen overvoltage of the zinc plating layer causes the non-uniform production of a hydrogen gas during the electropainting, and the thus non-uniformly produced hydrogen gas which is confined in the painting film causes craters in the painting film, thus resulting in a poorer cratering resistance of the zinc plated steel sheet (hereinafter referred to as the "problem 2").

It is a conventional practice, as a means for solving the problem 1, to apply a high-viscosity lubricant oil onto the surface of the zinc plated steel sheet prior to press-forming same to improve antifriction of the zinc plated steel sheet.

Application of the high-viscosity lubricant oil onto the surface of the zinc plated steel sheet as described above poses however the following problems:

(a) The high-viscosity lubricant oil contaminates the working place; and

(b) It is necessary to remove the high-viscosity lubricant oil applied onto the surface of the zinc plated steel sheet prior to applying painting thereto. This removing operation is not however easy. Complete removal of the high-viscosity lubricant oil requires much time and labor.

With regard to the frictional coefficient of a zinc electroplated steel sheet, the "Plating & Surface Finishing", March 1989, pp. 62-69 teaches as follows (hereinafter referred to as the "prior art"):

(i) Application of a conventional anticorrosive oil onto the surface of the zinc electroplating layer having crystals oriented along the (0001) plane, leads to a relatively large frictional coefficient thereof of 0.19; and

(ii) Application of a conventional anticorrosive oil onto the surface of the zinc electroplating layer having crystals oriented along the {10$\bar{1}$0} plane (where, X is 1, 2, 3 or 4), on the other hand, results in a small frictional coefficient thereof of 0.13.

Apart from the above-mentioned problems resulting from the application of the high-viscosity lubricant oil, the zinc electroplated steel sheet applied with the high-viscosity lubricant oil on the surface thereof has a small frictional coefficient of 0.11. If the orientation of the crystals of the zinc electroplating layer along the {10$\bar{1}$X} plane (where, X is 1, 2, 3 or 4) as taught by the prior art can be maintained, an antifriction of the same order as in the application of the high-viscosity lubricant oil would be available by the application of the conventional anticorrosive oil which is easy to remove, onto the surface of the zinc electroplated steel sheet.

However, the crystal orientation of the zinc electroplating layer of the zinc electroplated steel sheet

depends upon electroplating conditions, and among others, upon an electric current density. As a result, it is inevitable to alter the plating conditions in response to the width, for example, of the steel sheet to be electroplated. In the manufacture of the zinc electroplated steel sheet in an industrial scale, it is practically impossible to maintain the orientation of the crystals of the zinc electroplating layer along the (10$\bar{1}$0) plane (where, X is 1, 2, 3 or 4).

A means to solve the problem 2 has not as yet been proposed.

Under such circumstances, there is a strong demand for the development of a plated steel sheet excellent in antifriction, corrosion resistance and painting adaptability, but such a plated steel sheet has not as yet been proposed.

SUMMARY OF THE INVENTION

An object of the present invention is therefore to provide a plated steel sheet having two electroplating layers and excellent in antifriction, corrosion resistance and painting adaptability.

In accordance with one of the features of the present invention, there is provided a plated steel sheet having two plating layers and excellent in antifriction, corrosion resistance and painting adaptability, characterized by comprising;

a steel sheet;

a zinc plating layer formed on at least one surface of said steel sheet, said zinc plating layer having a plating weight within a range of from 25 to 150 g/m^2 per surface of said steel sheet; and

an electroplating layer formed on said zinc plating layer, said electroplating layer comprising at least one element selected from the group consisting of chromium, manganese, iron, cobalt and nickel, and said electroplating layer having a plating weight within a range of from 1 to 10 g/m^2 per surface of said steel sheet.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a graph illustrating, for the plated steel sheet of the present invention, which has a zinc plating layer as a lower layer formed on the surface of the steel sheet and an electroplating layer as an upper layer formed on the zinc plating layer, the relationship between a frictional coefficient of the plated steel sheet and a plating weight of the electroplating layer as the upper layer; and

Fig. 2 is a schematic front view illustrating an apparatus for measuring a frictional coefficient.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

From the above-mentioned point of view, extensive studies were carried out to develop a plated steel sheet having two plating layers and excellent in antifriction, corrosion resistance and painting adaptability.

As a result, the following findings were obtained:

A plated steel sheet having two plating layers and excellent in antifriction, corrosion resistance and painting adaptability is available by the following steps:

(1) forming a zinc plating layer on at least one surface of a steel sheet;

(2) limiting a plating weight of the zinc plating layer within a range of from 25 to 150 g/m^2 per surface of the steel sheet;

(3) forming an electroplating layer comprising at least one element selected from the group consisting of chromium, manganese, iron, cobalt and nickel, on the zinc plating layer; and

(4) limiting a plating weight of the electroplating layer within a range of from 1 to 10 g/m^2 per surface of the steel sheet.

The present invention was made on the basis of the above-mentioned findings. The plated steel sheet of the present invention having two plating layers and excellent in antifriction, corrosion resistance and plating adaptability is described below with reference to the drawings.

The plated steel sheet of the present invention excellent in antifriction, corrosion resistance and painting adaptability comprises a steel sheet, a zinc plating layer as a lower layer formed on at least one surface of the steel sheet and an electroplating layer as an upper layer formed on the zinc plating layer.

The zinc plating layer as the lower layer formed on at least one surface of the steel sheet has a function of imparting an excellent corrosion resistance to the plated steel sheet.

The zinc plating layer is formed by either of the electroplating method and the dip-plating method, which are now widely diffused as an industrialized processes. When forming the zinc plating layer by the electroplating method, a zinc electroplating bath is selected from among a bath containing sulfate, a bath

containing chloride and a bath containing a mixture of sulfate and chloride. When forming the zinc plating layer by the dip-plating method, any one of the commonly utilized zinc dip-plating baths is used.

The plating weight of the zinc plating layer as the lower layer exerts an important effect on corrosion resistance, antifriction and press-formability of the plated steel sheet. With a plating weight of the zinc plating layer of under 25 g/m^2 per surface of the steel sheet, a desired corrosion resistance necessary for a rust-preventive steel sheet used as a material for an automobile body is not available. With a plating weight of the zinc plating layer of over 150 g/m^2 per surface of the steel sheet, on the other hand, when forming same by the electroplating method, zinc crystals of the zinc electroplating layer become coarser. As a result, a uniform electroplating layer as the upper layer cannot be formed on the zinc electroplating layer, thus making it impossible to obtain an effect of improving antifriction described later by the electroplating layer as the upper layer. In addition, with a plating weight of the zinc plating layer of over 150 g/m^2 per surface of the steel sheet, when forming the zinc plating layer by the dip-plating method, a zinc deposition in the width direction of the steel sheet shows a very non-uniform distribution, thus making it difficult to conduct the press-forming of the plated steel sheet. The plating weight of the zinc plating layer as the lower layer should therefore be limited within a range of from 25 to 150 g/m^2 per surface of the steel sheet.

The electroplating layer as the upper layer, which is formed on the zinc plating layer as the lower layer and comprises at least one element selected from the group consisting of chromium, manganese, iron, cobalt and nickel, has a function of imparting an excellent painting adaptability as typically represented by a high cratering resistance and an excellent antifriction. Since all the above-mentioned elements have a high melting point, it is difficult to form a plating layer of these elements as the upper layer on the zinc plating layer by the dip-plating method. The electroplating layer of these elements as the upper layer is therefore formed by the electroplating method with the use of an electroplating bath such as a bath containing sulfate, a bath containing chloride, a bath containing a mixture of sulfate and chloride, or a bath containing borofluoride.

Fig. 1 is a graph illustrating, for the plated steel sheet of the present invention, which has a zinc plating layer as a lower layer formed on the surface of the steel sheet and an electroplating layer as an upper layer formed on the zinc plating layer, the relationship between a frictional coefficient of the plated steel sheet and a plating weight of the electroplating layer as the upper layer. More particularly, a zinc electroplating layer as a lower layer having a plating weight of 60 g/m^2 per surface of a steel sheet was formed by the electroplating method on one surface of the steel sheet. Then, a nickel electroplating layer as an upper layer was formed on the zinc electroplating layer by the electroplating method while changing the plating weight of the nickel electroplating layer. A frictional coefficient was measured for the plated steel sheet having the thus formed two plating layers.

As is clear from Fig. 1, when the plating weight of the nickel electroplating layer as the upper layer is under 1 g/m^2 per surface of the steel sheet, the plated steel sheet has a high frictional coefficient. When the plating weight of the nickel electroplating layer as the upper layer is over 10 g/m^2 per surface of the steel sheet, on the other hand, the plated steel sheet has a constant frictional coefficient at a level of up to 0.1, which does not decrease to below this level. This applies, not only to the case where the above-mentioned nickel electroplating layer is formed as the upper layer, but also to the case where an electroplating layer comprising at least one element selected from the group consisting of chromium, manganese, iron, cobalt and nickel is formed as the upper layer.

When the plating weight of the electroplating layer as the upper layer is under 1 g/m^2 per surface of the steel sheet, the frictional coefficient of the plated steel sheet is high as described above, so that antifriction of the plated steel sheet is deteriorated. When the plating weight of the electroplating layer as the upper layer is over 10 g/m^2 per surface of the steel sheet, on the other hand, the frictional coefficient of the plated steel sheet becomes constant at a level of up to 0.1.

As a result, not only the effect of the electroplating layer of improving antifriction of the plated steel sheet is saturated, but also corrosion resistance of the plated steel sheet becomes poorer. The plating weight of the electroplating layer as the upper layer, which comprises at least one element selected from the group consisting of chromium, manganese, iron, cobalt and nickel, should therefore be limited within a range of from 1 to 10 g/m^2 per surface of the steel sheet.

As described above, an excellent antifriction is imparted to the plated steel sheet, by forming the electroplating layer as the upper layer, which has a plating weight within a range of from 1 to 10 g/m^2 per surface of the steel sheet and comprises at least one element selected from the group consisting of chromium, manganese, iron, cobalt and nickel, on the zinc plating layer as the lower layer. The reason of this is estimated to be as follows:

The zinc plating layer of the zinc plated steel sheet has a relatively low hardness. Therefore, the zinc plating layer having a low hardness is deformed upon the press-forming of the zinc plated steel sheet. As a

result, a contact area between the zinc plating layer and the pressing portion of a press becomes larger, leading to a higher frictional coefficient of the zinc plated steel sheet. Antifriction of the zinc plated steel sheet therefore becomes lower. On the other hand, both a cold-rolled steel sheet and a zinc alloy plating layer of a zinc alloy plated steel sheet have a high hardness.

When the cold-rolled steel sheet or the zinc alloy plated steel sheet is press-formed, therefore, the surface of the cold-rolled steel sheet or the zinc alloy plating layer are hard to deform. As a result, a small contact area between the surface of the cold-rolled steel sheet or the zinc plating layer and the pressing portion of the press leads to a low frictional coefficient. The cold-rolled steel sheet or the zinc alloy plated steel sheet is therefore excellent in antifriction. The above description suggests that a higher hardness of the surface of a steel sheet provides a more excellent antifriction of the steel sheet.

In the present invention, the electroplating layer as the upper layer has a remarkably higher hardness than that of the zinc plating layer as the lower layer. When the plated steel sheet of the present invention is press-formed, therefore, the zinc plating layer as the lower layer deforms because of the low hardness thereof, and the electroplating layer as the upper layer is hard to deform because of the high hardness thereof. As a result, a small contact area between the surface of the electroplating layer and the pressing portion of the press leads to a low frictional coefficient of the plated steel sheet. The plated steel sheet of the present invention is therefore excellent in antifriction.

More particularly, when the plating weight of the electroplating layer as the upper layer is under 1 g/m^2 per surface of the steel sheet, most part of the surface of the zinc plating layer as the lower layer is exposed, and the contact area between the electroplated steel sheet and the pressing portion of the press becomes larger. This results in a high frictional coefficient of the plated steel sheet as in the above-mentioned zinc plated steel sheet. According as the plating weight of the electroplating layer as the upper layer increases from 1 g/m^2 per surface of the steel sheet, the electroplating layer as the upper layer more sufficiently covers the zinc plating layer as the lower layer, thus eliminating the exposed part of the zinc plating layer as the lower layer. This results in a smaller contact area between the plated steel sheet and the pressing portion of the press. As a result, the frictional coefficient of the plated steel sheet becomes very low. As described above, a plating weight of the electroplating layer as the upper layer of over 10 g/m^2 per surface of the steel sheet results in a constant frictional coefficient at a low level, which no longer decreases from this level.

In addition, the electroplating layer as the upper layer, which comprises at least one element selected from the group consisting of chromium, manganese, iron, cobalt and nickel, imparts an excellent painting adaptability, i.e., an excellent cratering resistance to the plated steel sheet.

More specifically, a hydrogen gas, if produced non-uniformly when forming a painting film by the electropainting on the surface of the plated steel sheet, is confined in the painting film, thus resulting in the occurrence of craters in the painting film.

However, since the electroplating layer as the upper layer of the plated steel sheet of the present invention, which comprises at least one element selected from the group consisting of chromium, manganese, iron, cobalt and nickel, has a low hydrogen overvoltage, a hydrogen gas is uniformly produced when forming a painting film by the electropainting. This results in a very rare occurrence of craters in the painting film, thus leading to an excellent painting adaptability, i.e., an excellent cratering resistance of the plated steel sheet.

Now, the plated steel sheet of the present invention having the two plating layers and excellent in antifriction, corrosion resistance and painting adaptability, is described further in detail by means of examples while comparing with examples for comparison.

EXAMPLES

Each of cold-rolled steel sheets having a thickness of 0.7 mm was subjected to a conventional degreasing treatment and a conventional pickling treatment to remove rust from the both surfaces thereof. Then, the steel sheet from the both surfaces of which rust was thus removed, was subjected to an electroplating under the conditions shown in Table 1 to form a zinc electroplating layer as a lower layer on each of the both surfaces of the steel sheet. In parallel with the above-mentioned electroplating, each of another cold-rolled steel sheets having a thickness of 0.7 mm, from the both surfaces of which rust was removed by the same method as described above, was subjected to a dip-plating under the following conditions to form a zinc dip-plating layer as a lower layer on each of the both surfaces of the steel sheet:

(a) Cold-rolled steel sheet : Ti-IF steel.

(b) Plating equipment: Continuous zinc dip-plating equipment having an annealing facility in the line.

(c) Plating bath: Zinc dip-plating bath containing aluminum in an amount of 0.14 wt.%.

(d) Plating bath temperature: 460 °C,

(e) Annealing temperature : 850 °C.

The plating weight was controlled by the gas squeezing method.

Then, each of the steel sheets having the zinc electroplating layer or the zinc dip-plating layer formed on each of the both surfaces thereof, was subjected to another electroplating under another conditions shown also in Table 1 to form an electroplating layer as an upper layer, which comprised at least one element selected from the group consisting of chromium, manganese, iron, cobalt and nickel, on the zinc electroplating layer or the zinc dip-plating layer. Thus, samples of the electroplated steel sheet within the scope of the present invention (hereinafter referred to as the "samples of the invention") Nos. 1 to 54 were prepared.

For each of the samples of the invention Nos. 1 to 54, the plating weight per surface of the steel sheet of the zinc electroplating layer or the zinc dip-plating layer, elements and the contents thereof of the electroplating layer, and the plating weight per surface of the steel sheet of the electroplating layer are shown also in Table 1.

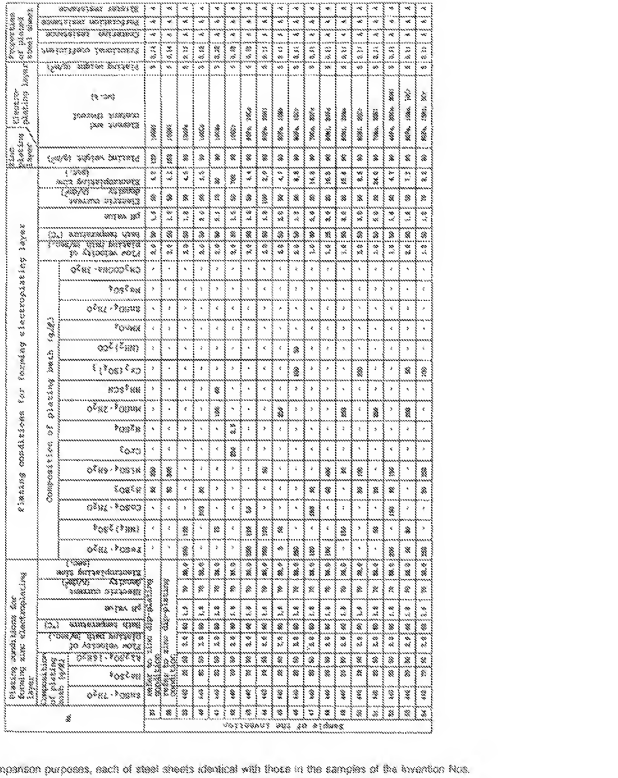
Table 1 (2)

	No.	Plating conditions for forming zinc electroplating layer: Composition of plating bath (g/ℓ): $ZnSO_4\cdot7H_2O$	Na_2SO_4	$Al_2(SO_4)_3\cdot18H_2O$	Flow velocity of plating bath (m/sec.)	Bath temperature (°C)	pH value	Electric current density (A/dm²)	Electroplating time (sec.)	Plating conditions for forming electroplating layer: Composition of plating bath (g/ℓ): $FeSO_4\cdot7H_2O$	$(NH_4)_2SO_4$	$CoSO_4\cdot7H_2O$	H_3BO_3	$NiSO_4\cdot6H_2O$	CrO_3	H_2SO_4	$MnSO_4\cdot2H_2O$	NH_4SCN	$Cr_2(SO_4)_3$	$(NH_2)_2CO$	$KMnO_4$	$ZnSO_4\cdot7H_2O$	Na_2SO_4	$CH_3COONa\cdot3H_2O$	Flow velocity of plating bath (m/sec.)	Bath temperature (°C)	pH value	Electric current density (A/dm²)	Electroplating time (sec.)	Zinc plating layer: Plating weight (g/m²)	Electroplating layer: Element and content thereof (wt.%)	Plating weight (g/m²)	Properties of plated steel sheet: Frictional coefficient	Cratering resistance	Perforation corrosion resistance	Blister resistance
Sample of the invention	1	440	30	30	2.0	60	1.5	70	25.2	200	100	-	-	-	-	-	-	-	-	-	-	-	-	-	2.0	50	1.5	50	3.5	40	100Fe	3	0.12	A	A	A
	2	440	30	30	2.4	60	1.5	70	25.3	-	-	300	30	-	-	-	-	-	-	-	-	-	-	-	2.0	50	5.0	50	1.9	40	100Co	3	0.11	A	A	A
	3	440	30	30	2.8	60	1.5	70	25.3	-	-	-	30	300	-	-	-	-	-	-	-	-	-	-	2.0	50	1.5	50	1.7	40	100Ni	4	0.11	A	A	A
	4	440	30	30	2.0	60	1.5	70	25.2	-	75	-	-	-	-	-	100	50	-	-	-	-	-	-	2.2	50	4.1	10	12.8	40	100Mn	3	0.11	A	A	A
	5	440	30	30	2.0	60	1.5	70	25.2	-	-	-	-	-	250	2.5	-	-	-	-	-	-	-	-	2.0	50	1.5	50	400	40	100Cr	2	0.15	A	A	A
	6	440	30	30	2.4	60	1.5	70	25.2	200	100	50	-	-	-	-	-	-	-	-	-	-	-	-	2.0	50	1.8	50	2.5	40	80Fe, 20Co	3	0.12	A	A	A
	7	440	30	30	2.0	60	1.9	70	25.3	250	150	-	-	30	-	-	-	-	-	-	-	-	-	-	2.0	50	1.8	100	1.9	40	90Fe, 10Ni	3	0.12	A	A	A
	8	440	30	30	2.0	60	1.8	70	25.1	5	50	-	-	-	-	-	200	-	-	-	-	-	-	-	2.2	50	2.0	50	2.8	40	90Fe, 10Mn	5	0.11	A	A	A
	9	440	30	30	2.0	60	1.8	70	25.1	250	-	-	-	-	-	-	-	-	100	50	-	-	-	-	2.0	50	1.2	50	2.3	40	90Fe, 10Cr	5	0.13	A	A	A
	10	440	30	30	2.0	60	1.5	70	25.2	100	-	250	30	-	-	-	-	-	-	-	-	-	-	-	2.0	50	5.0	50	3.8	40	70Co, 30Fe	2	0.11	A	A	A
	11	440	30	30	2.4	60	1.5	70	25.2	150	-	300	50	-	-	-	-	-	-	-	-	-	-	-	2.0	50	3.0	50	2.5	50	60Co, 40Fe	3	0.11	A	A	A
	12	440	30	30	2.0	60	1.5	70	25.2	-	50	5	-	-	-	-	250	-	-	-	-	-	-	-	2.0	25	3.5	10	21.0	40	90Mn, 10Co	3	0.11	A	A	A
	13	440	30	30	2.0	60	1.8	70	25.3	-	-	100	30	-	-	-	-	-	150	-	-	-	-	-	2.2	50	3.5	50	1.5	40	90Co, 10Cr	5	0.11	A	A	A
	14	440	30	30	2.0	60	1.5	70	25.2	100	-	-	30	100	-	-	-	-	-	-	-	-	-	-	2.0	25	3.0	30	4.5	50	80Ni, 20Fe	2	0.11	A	A	A
	15	440	30	30	2.4	60	1.5	70	25.2	-	-	120	60	400	-	-	-	-	-	-	-	-	-	-	2.0	25	3.0	30	4.5	50	80Ni, 20Co	2	0.11	A	A	A
	16	440	30	30	2.4	60	1.5	70	25.3	-	100	-	-	30	-	-	250	-	-	-	-	-	-	-	2.0	50	3.0	30	5.2	50	80Mn, 20Ni	3	0.11	A	A	A
	17	440	30	30	2.0	60	1.8	70	25.1	-	-	-	30	100	-	-	-	-	250	-	-	-	-	-	2.0	50	3.0	50	4.3	40	80Ni, 20Cr	5	0.13	A	A	A
	18	440	30	30	2.4	60	1.5	70	25.2	30	90	-	-	-	-	-	250	-	-	-	-	-	-	-	2.0	50	3.0	30	12.5	50	75Mn, 25Fe	2	0.11	A	A	A

Table 1 (2)

	No.	Plating conditions for forming zinc electroplating layer: Composition of plating bath (g/ℓ): $ZnSO_4 \cdot 7H_2O$	Na_2SO_4	$Al_2(SO_4)_3 \cdot 18H_2O$	Flow velocity of plating bath (m/sec.)	Bath temperature (°C)	pH value	Electric current density (A/dm²)	Electroplating time (sec.)	Plating conditions for forming electroplating layer: Composition of plating bath (g/ℓ): $FeSO_4 \cdot 7H_2O$	$(NH_4)_2SO_4$	$CoSO_4 \cdot 7H_2O$	H_3BO_3	$NiSO_4 \cdot 6H_2O$	CrO_3	H_2SO_4	$MnSO_4 \cdot 5H_2O$	NH_4SCN	$Cr_2(SO_4)_3$	$(NH_2)_2CO$	$KMnO_4$	$SnSO_4 \cdot 7H_2O$	Na_2SnO_3	$CH_3COONa \cdot 3H_2O$	Flow velocity of plating bath (m/sec.)	Bath temperature (°C)	pH value	Electric current density (A/dm²)	Electroplating time (sec.)	Zinc plating layer: Plating weight (g/m²)	Electroplating layer: Element and content thereof (wt.%)	Plating weight (g/m²)	Properties of plated steel sheet: Frictional coefficient	Cratering resistance	Perforation resistance	Blister resistance
Sample of the invention	19	440	30	50	2.0	60	1.5	70	25.3	-	30	30	-	-	-	-	200	-	-	-	-	-	-	-	1.0	50	3.0	30	10.0	60	70Mn, 30Co	3	0.11	A	A	A
	20	440	30	50	2.0	60	1.8	70	25.3	-	30	-	30	-	-	-	200	-	-	-	-	-	-	-	1.0	50	5.0	30	14.2	60	70Mn, 30B	3	0.11	A	A	A
	21	440	30	50	2.0	60	1.8	70	25.3	-	-	-	-	-	30	2.2	-	-	-	-	100	-	-	-	1.0	50	5.0	30	7.5	60	70Mn, 30Cr	3	0.11	A	A	A
	22	440	30	50	2.0	60	1.5	70	25.3	50	-	-	-	-	-	-	-	-	200	30	-	-	-	-	2.0	50	3.0	30	2.9	60	80Cr, 20Fe	3	0.11	A	A	A
	23	440	30	50	2.0	60	1.5	70	25.5	-	-	30	30	-	-	-	-	-	200	-	-	-	-	-	2.0	50	3.0	30	3.5	60	80Cr, 20Co	3	0.11	A	A	A
	24	440	30	50	2.0	60	1.8	70	25.3	-	-	-	30	50	-	-	-	-	200	-	-	-	-	-	2.0	50	3.0	50	4.2	60	80Cr, 20Ni	3	0.11	A	A	A
	25	440	30	50	2.0	60	1.8	70	25.3	-	-	-	-	-	200	2	-	-	-	-	100	-	-	-	2.0	50	3.0	50	5.3	60	60Cr, 40Mn	3	0.11	A	A	A
	26	440	30	50	2.0	60	1.8	70	25.3	200	-	150	30	150	-	-	-	-	-	-	-	-	-	-	1.5	50	1.8	50	2.5	60	40Fe, 30Co, 30Ni	3	0.11	A	A	A
	27	440	30	50	2.0	60	1.8	70	25.3	50	30	-	-	-	-	-	200	-	30	-	-	-	-	-	2.0	50	1.8	30	4.9	60	80Mn, 10Fe, 10Cr	3	0.11	A	A	A
	28	440	30	50	2.0	60	1.5	70	25.3	200	-	-	30	200	-	-	-	-	100	-	-	-	-	-	1.0	50	1.0	70	3.8	60	80Fe, 10Ni, 10Cr	3	0.11	A	A	A
	29	440	30	50	2.0	60	1.5	70	25.3	-	-	-	-	150	-	-	200	-	100	-	-	-	30	20	2.0	50	1.8	30	11.0	60	80Mn, 10Ni, 10Sn	3	0.11	A	A	A
	30	440	30	50	2.0	60	1.8	70	25.3	10	-	-	-	-	-	-	200	-	10	-	-	-	30	20	2.0	50	1.8	30	9.2	60	80Mn, 10Fe, 10Sn	3	0.11	A	A	A
	31	440	30	50	2.0	60	1.8	70	25.3	-	-	-	30	300	-	-	-	-	-	-	-	-	-	-	2.0	50	1.8	30	1.9	60	100Ni	3	0.11	A	A	A
	32	440	30	50	2.0	60	1.5	70	25.3	-	-	-	30	300	-	-	-	-	-	-	-	-	-	-	2.0	50	1.8	50	4.2	50	100Ni	3	0.11	A	A	A
	33	440	30	50	2.0	60	1.5	70	25.3	-	-	-	30	300	-	-	-	-	-	-	-	-	-	-	2.0	50	1.8	50	8.8	60	100Ni	10	0.09	A	A	A
	34	440	30	50	2.0	60	1.8	50	16.3	-	-	-	30	300	-	-	-	-	-	-	-	-	-	-	2.0	50	1.8	50	2.5	20	100Ni	2	0.10	A	B	C
	35	440	30	50	2.0	60	1.5	70	12.7	-	-	-	30	300	-	-	-	-	-	-	-	-	-	-	2.0	50	1.8	50	2.5	50	100Ni	3	0.11	A	B	C
	36	440	30	50	2.0	60	1.8	70	25.0	-	-	-	30	300	-	-	-	-	-	-	-	-	-	-	2.0	50	1.8	50	4.2	50	100Ni	3	0.12	A	A	A

Table 1 (3)



For comparison purposes, each of steel sheets identical with those in the samples of the invention Nos. 1 to 54 (except for Nos. 37 and 38), was subjected to a conventional degreasing treatment and a conventional pickling treatment to remove rust from the both surfaces thereof. Then, the steel sheet from the both surfaces of which rust was thus removed, was subjected to an electroplating under the conditions shown in Table 2 to form a zinc electroplating layer as a lower layer on each of the both surfaces of the

steel sheet.

Then, each of the steel sheets having the zinc electroplating layer formed on each of the both surfaces thereof, was subjected to another electroplating under another conditions shown also in Table 2 to form an electroplating layer as an upper layer on the zinc electroplating layer. Thus, samples of the electroplated steel sheet outside the scope of the present invention (hereinafter referred to as the "samples for comparison") Nos. 1 to 7 were prepared. Each of the samples for comparison Nos. 1 and 7 had only a zinc electroplating layer as a single layer.

The plating weight per surface of the steel sheet of the zinc electroplating layer as the lower layer for each of the samples for comparison Nos. 1 to 7, as well as elements and the contents thereof of the electroplating layer as the upper layer, and the plating weight per surface of the steel sheet of the above-mentioned electroplating layer for each of the samples for comparison Nos. 2 to 6 are also shown in Table 2.

Table 2

No.	Zinc layer bath: $ZnSO_4 \cdot 7H_2O$ (g/l)	Zinc layer bath: Na_2SO_4 (g/l)	Zinc layer bath: $Al_2(SO_4)_3 \cdot 18H_2O$ (g/l)	Zinc layer: Flow velocity of plating bath (m/sec.)	Zinc layer: Bath temperature (°C)	Zinc layer: pH value	Zinc layer: Electric current density (A/dm²)	Zinc layer: Electroplating time (sec.)	$FeSO_4 \cdot 7H_2O$	$(NH_4)_2SO_4$	$CoSO_4 \cdot 7H_2O$	H_3BO_3	$NiSO_4 \cdot 6H_2O$	CrO_3	H_2SO_4	$MnSO_4 \cdot 3H_2O$	NH_4SCN	$Cr_2(SO_4)_3$	$(NH_2)_2CO$	$KMnO_4$	$ZnSO_4 \cdot 7H_2O$	Na_2SO_4	$CH_3COONa \cdot 3H_2O$	Electroplating layer: Flow velocity of plating bath (m/sec.)	Electroplating layer: Bath temperature (°C)	Electroplating layer: pH value	Electroplating layer: Electric current density (A/dm²)	Electroplating layer: Electroplating time (sec.)	Zinc plating layer: Plating weight (g/m²)	Electroplating layer: Element and content thereof (wt.%)	Electroplating layer: Plating weight (g/m²)	Frictional coefficient	Cratering resistance	Perforation resistance	Blister resistance
Sample for comparison 1	440	30	30	2.0	50	1.5	70	25.8	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	60	—	-	0.20	4	4	4
2	440	30	30	2.0	60	1.8	70	25.3	-	-	-	30	300	-	-	-	-	-	-	-	-	-	-	2.0	50	1.8	50	1.5	60	100Ni	0.5	0.19	4	5	4
3	440	30	30	2.0	50	1.5	70	12.7	-	-	-	30	300	-	-	-	-	-	-	-	-	-	-	2.0	50	1.5	50	19.5	60	100Ni	30	0.08	4	3	3
4	440	30	30	2.0	50	1.5	70	25.2	200	-	-	-	-	-	-	-	-	-	-	-	175	30	30	2.0	50	1.2	50	4.7	60	85Zn, 15Fe	5	0.16	2	4	5
5	440	30	30	2.0	50	1.5	70	25.9	-	-	-	-	225	-	-	-	-	-	-	-	175	60	-	2.0	50	1.2	50	4.5	60	88Zn, 12Ni	5	0.18	2	4	4
6	440	30	30	2.0	50	1.5	70	4.5	-	-	-	30	300	-	-	-	-	-	-	-	-	-	-	2.0	50	1.5	50	2.6	15	100Ni	3	0.19	4	2	2
7	440	30	30	2.0	50	1.5	70	25.8	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	60	—	-	0.13	4	4	4

Then, for each of the thus prepared samples of the invention Nos. 1 to 54 and the samples for comparison Nos. 1 to 7, antifriction, corrosion resistance and painting adaptability were investigated by means of performance tests as described below. The results of these tests are shown also in Tables 1 and 2.

(1) Antifriction test:

A mineral oil type anticorrosive oil for a steel sheet (product name: NOX RUST 530F40) manufactured by Parker Industries, Inc. was applied onto one surface of each of the samples of the invention Nos. 1 to 54 and the samples for comparison Nos. 1 to 6, and a high-viscosity lubricant oil (product name: FERRDCOTE 61-MAL-HCL-1) manufactured by Nippon Quaker Chemical Co., Ltd. was applied onto one surface of the sample for comparison No. 7. The frictional coefficient of each sample on one surface of which the anticorrosive oil was applied and the frictional coefficient of the sample for comparison No. 7 on one surface of which the high-viscosity lubricant was applied, were measured with the use of an apparatus as shown in Fig. 2, thereby evaluating antifriction of each sample on the basis of the thus measured frictional coefficient.

The apparatus for measuring frictional coefficient of the sample comprised, as shown in Fig. 2, a rack 2; a supporting stand 5, provided on the rack 2 vertically movably along a plurality of guide rods 12 and 13 attached vertically to the rack 2, and having a plurality of rollers 6 on the upper end thereof; a supporting stand driving mechanism (not shown) for vertically moving the supporting stand 5; a first load cell 8, provided between the supporting stand 5 and the rack 2, for measuring the force applied vertically to the supporting stand 5; a pressing block 4 fitted to a frame 3 fixed to the rack 2 so as to project toward the supporting stand 5; a horizontally movable sliding table 7 mounted on the rollers 6 of the supporting stand 5 between the supporting stand 5 and the pressing block 4; a sliding table driving mechanism (not shown), provided on another rack 11, for horizontally moving the sliding table 7, and a second load cell 9, provided between an operating rod 10 connected to the sliding table driving mechanism and one end of the sliding table 7, for measuring the force applied horizontally to the sliding table 7.

By operating the supporting stand driving mechanism, the supporting stand 5 was moved upward to lift up the sliding table 7 on the upper surface of which a sample 1 was placed. Thus the upper surface of the sample 1 was pressed against the lower end of the pressing block 4, and the force N applied in the arrow A direction was measured by means of the first load cell 8. Then, by operating the sliding table driving mechanism, the sliding table 7 was horizontally moved in the arrow B direction, together with the sample 1 placed on the upper surface thereof, and the force F applied in the arrow B direction to the sliding table 7 was measured by means of the second load cell 9, at the moment when the sliding table 7 reached the moving speed of 1 m/minute. The ratio of the force F to the force N, i.e., the ratio F/N was determined, and the thus determined value was used as the value of frictional coefficient.

(2) Cratering resistance test:

Each of the samples having a width of 70 mm and a length of 150 mm was subjected to a dipping type phosphating for a steel sheet for automobile in a phosphating solution (product name: PBL 3080) manufactured by Nihon Parkerizing Co., Ltd., to form a phosphate film on the surface of the sample. Then, the sample was subjected to a cation type electropainting with the use of a paint (product name: ELECRON 9400) manufactured by Kansai Paint Co., Ltd. under the following conditions to form a painting film having a thickness of 20 µm on the phosphate film:

(a) Impressed voltage: 280 V,
(b) Area ratio between anode and cathode: 1:1,
(c) Electrification: instantaneous one,
(d) Electrifying time: 3 minutes.

Cratering resistance was evaluated by means of the number of craters produced in the painting film during the formation of the painting film as described above. The criteria for evaluation were as follows:

A: up to ten craters produced within a circle of a diameter of 40 mm at the center of the sample,
B: from 11 to 100 such craters,
C: at least 101 such craters.

(3) Corrosion resistance test:

Corrosion resistance was evaluated by means of perforation resistance and blister resistance as follows:

(a) Perforation resistance:

As in the cratering resistance test as described above, a phosphate film was formed on the surface of each of the samples, and a painting film having a thickness of 20 µm was formed on the phosphate film by means of the electropainting. Then, a notch was provided in the thus formed painting film. Each of the

samples having the thus notched painting film was then subjected to 60 cycles of corrosion tests, each cycle comprising a salt water spray, a drying, a dipping into salt water, and a drying for 24 hours. Then, the painting film and corrosion products produced during the corrosion test, were removed from each sample thus subjected to the 60 cycles of corrosion tests, and the maximum corrosion depth produced in the steel sheet was measured. Perforation resistance was evaluated by means of the thus measured maximum corrosion depth. The criteria for evaluation were as follows:

A: A maximum corrosion depth of under 0.1 mm,
B: A maximum corrosion depth within a range of from 0.1 to under 0.2 mm,
C: A maximum corrosion depth within a range of from 0.2 to under 0.4 mm, and
D: A maximum corrosion depth of at least 0.4 mm.

(b) Blister resistance:

As in the cratering resistance test as described above, a phosphate film was formed on the surface of each of the samples, and a lower painting film having a thickness of 10 µm was formed on the phosphate film by means of the electropainting. Then, an intermediate painting film having a thickness of 35 µm and an upper painting film having a thickness of 35 µm were formed on the thus formed lower painting film. Then, a notch was provided on the thus formed triple-layer painting film. A salt spray test was carried out on each of the samples having the thus notched triple-layer painting film. More specifically, each sample was exposed to the open air for a period of one year, during which salt water having a sodium chloride content of 5 wt.% was sprayed over the sample at a rate of twice a week. Then, the maximum blister width of the painting film was measured on one side of the notch on the sample after the salt spray test, and blister resistance was evaluated by means of the thus measured maximum blister width of the painting film. The criteria for evaluation were as follows:

A: A maximum blister width of under 1 mm;
B: A maximum blister width within a range of from 1 mm to under 2 mm;
C: A maximum blister width within a range of from 2 mm to under 2.5 mm; and
D: A maximum blister width of at least 2.5 mm.

As is clear from Table 1, all the samples of the invention Nos. 1 to 54 had a frictional coefficient of up to 0.16, and were therefore excellent in antifriction.

All the samples of the invention Nos. 1 to 54 were excellent in painting adaptability as typically represented by a high cratering resistance with the number of craters of up to 10 produced within a circle of a diameter of 40 mm at the center of the sample, as evaluated by A.

In terms of perforation resistance and blister resistance, which represented corrosion resistance, although the samples of the invention Nos. 34 and 35 were slightly poor, all the other samples of the invention were excellent. Each of the samples of the invention Nos. 34 and 35 was slightly inferior in corrosion resistance to each of the samples of the invention Nos. 1 to 33 and 36 to 54 because the plating weight of the zinc electroplating layer of each of the samples of the invention Nos. 34 and 35 was smaller than that of each of the samples of the invention Nos. 1 to 33 and 36 to 54.

As is evident from the above description, all the samples of the invention Nos. 1 to 54 were excellent in antifriction, corrosion resistance and painting adaptability

As is clear from Table 2, in contrast, none of the samples for comparison Nos. 1 to 7 satisfied simultaneously the following three favorable merits possessed by each of the samples of the invention Nos. 1 to 54:

(i) a frictional coefficient of up to 0.18 in the antifriction test;
(ii) a maximum blister width of under 2.5 mm and a maximum corrosion depth of under 0.4 mm in the corrosion test; and
(iii) a number of craters representing painting adaptability of up to 10 in the cratering resistance test.

More particularly, the sample for comparison No. 1 having the zinc electroplating layer as the single layer and applied with the anticorrosive oil for a steel sheet on the surface thereof had a large frictional coefficient of 0.3. The sample for comparison No. 2 having a low plating weight of the nickel electroplating layer as the upper layer outside the scope of the present invention had a large frictional coefficient of 0.28. The sample for comparison No. 3 having a high plating weight of the nickel electroplating layer as the upper layer outside the scope of the present invention was poor in perforation resistance and blister resistance.

The sample for comparison No. 4 having the zinc-iron alloy electroplating layer as the upper layer and the sample for comparison No. 5 having the zinc-nickel alloy electroplating layer as the upper layer, which were outside the scope of the present invention in that the electroplating layer as the upper layer contained zinc, were poor in cratering resistance. The sample for comparison No. 6 having a low plating weight of the zinc

electroplating layer as the lower layer outside the scope of the present invention was poor in perforation resistance and blister resistance.

Furthermore, a high-viscosity lubricant oil (product name: FERROCOTE 61-MAL-HCL-1) manufactured by Nippon Quaker Chemical Co., Ltd. was applied onto the zinc electroplating layer as the single layer of the sample for comparison No. 7, and an antifriction test as described above was effected on the sample for comparison No. 7 applied with the high-viscosity lubricant oil on the zinc electroplating layer thereof. The above-mentioned sample for comparison No. 7 had a frictional coefficient of 0.11. This revealed that the samples of the invention Nos. 1 to 54 applied with the easily removable anticorrosive oil had substantially the same antifriction as that of the sample for comparison No. 7 applied with the high-viscosity lubricant oil which was very difficult to remove.

According to the present invention, as described above in detail, it is possible to provide a plated steel sheet having two plating layers and excellent in antifriction, corrosion resistance and painting adaptability, thus providing industrially useful effects.

Claims

1. A plated steel sheet having two plating layers and excellent in antifriction, corrosion resistance and painting adaptability, characterized by comprising:

   a steel sheet;

   a zinc plating layer formed on at least one surface of said steel sheet, said zinc plating layer having a plating weight within a range of from 25 to 150 g/m^2 per surface of said steel sheet; and

   an electroplating layer formed on said zinc plating layer, said electroplating layer comprising at least one element selected from the group consisting of chromium, manganese, iron, cobalt and nickel, and said electroplating layer having a plating weight within a range of from 1 to 10 g/m^2 per surface of said steel sheet.

2. A plated steel sheet as claimed in Claim 1, wherein:
   said zinc plating layer is an zinc electroplating layer.

3. A plated steel sheet as claimed in Claim 1, wherein:
   said zinc plating layer is a zinc dip-plating layer.

4. A plated steel sheet as claimed in any one of Claims 1 to 3, wherein:
   said electroplating layer comprises chromium.

5. A plated steel sheet as claimed in any one of Claims 1 to 3, wherein:
   said electroplating layer comprises manganese.

6. A plated steel sheet as claimed in any one of Claims 1 to 3, wherein:
   said electroplating layer comprises iron.

7. A plated steel sheet as claimed in any one of Claims 1 to 3, wherein:
   said electroplating layer comprises cobalt.

8. A plated steel sheet as claimed in any one of Claims 1 to 3, wherein:
   said electroplating layer comprises nickel.

9. A plated steel sheet as claimed in any one of Claims 1 to 3, wherein:
   said electroplating layer comprises iron and cobalt.

10. A plated steel sheet as claimed in any one of Claims 1 to 3, wherein:
    said electroplating layer comprises iron and nickel.

11. A plated steel sheet as claimed in any one of Claims 1 to 3, wherein:
    said electroplating layer comprises iron and manganese

12. A plated steel sheet as claimed in any one of Claims 1 to 3, wherein: said electroplating layer comprises iron and chromium.

13. A plated steel sheet as claimed in any one of Claims 1 to 3, wherein: said electroplating layer comprises cobalt and nickel.

14. A plated steel sheet as claimed in any one of Claims 1 to 3, wherein: said electroplating layer comprises cobalt and manganese.

15. A plated steel sheet as claimed in any one of Claims 1 to 3, wherein: said electroplating layer comprises cobalt and chromium.

16. A plated steel sheet as claimed in any one of Claims 1 to 3, wherein: said electroplating layer comprises nickel and manganese.

17. A plated steel sheet as claimed in any one of Claims 1 to 3, wherein: said electroplating layer comprises nickel and chromium.

18. A plated steel sheet as claimed in any one of Claims 1 to 3, wherein: said electroplating layer comprises manganese and chromium.

19. A plated steel sheet as claimed in any one of Claims 1 to 3, wherein: said electroplating layer comprises iron, cobalt and nickel.

20. A plated steel sheet as claimed in any one of Claims 1 to 3, wherein: said electroplating layer comprises iron, manganese and chromium.

21. A plated steel sheet as claimed in any one of Claims 1 to 3, wherein: said electroplating layer comprises iron, nickel and chromium.

22. A plated steel sheet as claimed in any one of Claims 1 to 3, wherein: said electroplating layer comprises nickel, manganese and chromium.

FIG. 1

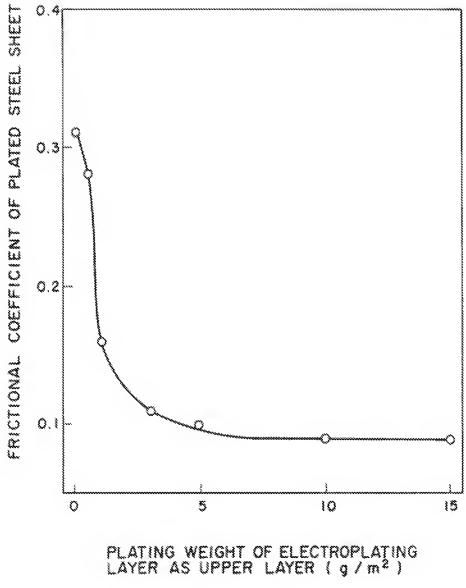
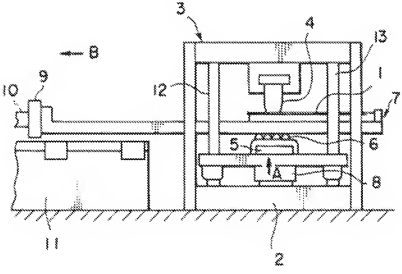

FRICTIONAL COEFFICIENT OF PLATED STEEL SHEET
0.4
0.3
0.2
0.1
0
5
10
15
PLATING WEIGHT OF ELECTROPLATING LAYER AS UPPER LAYER (g / m²)

FIG. 2



European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 91 10 6540

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	PATENT ABSTRACTS OF JAPAN vol. 8, no. 114 (C-225)(1551) 26 May 1984 & JP-A-59 025 992 (KAWASAKI SEITETSU KK) 10 February 1984 * abstract *	1,2,15	C25D5/10
X	GB-A-2 161 499 (PHENIX WORKS) * page 2, line 30 - line 65 * * page 2; claim 3 *	1,3,4,5,6,7,8	
X	US-A-3 323 661 (NELSON) * column 3, line 30 - line 48; claims 3,4 *	1,2,3,4	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C25D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	18 DECEMBER 1991	NGUYEN THE NGHIEP N.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P0401)